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DANQUIGNY, Alain School of Chemistry, University of Southampton, UK, 11 April–10 June 2006

Scope of Research

Fundamental studies are being conducted for creation of new functional materials with novel structures and properties. The major subjects are: organo-chemical transformation of fullerenes C_{60} and C_{70} , specifically organic synthesis of endohedral fullerenes by the technique of molecular surgery; generation of alkylated fullerene cations and their application for the synthesis of functional material; synthesis of new redox-active π -systems.

Research Activities (Year 2006)

Presentations

Synthesis and Properties of Fullerene C_{70} Encapsulating Hydrogen Molecule(s), Murata Y, Maeda S, Murata M, Komatsu K, 209th Meeting of the Electrochemical Society, 10 May 2006, Denver, USA.

Organic Synthesis of Endohedral Fullerenes by Molecular Surgery, Murata Y, 18th Symposium on Fundamental Organic Chemistry, 8 October 2006, Fukuoka, Japan (Invited).

Fine Tuning of the Orifice Size: Synthesis of an Open-cage Fullerene Containing Selenium at the Rim of the Orifice and Insertion of Molecular Hydrogen, Murata Y, Chuang S-C, Komatsu K, The 10th International Kyoto Conference on New Aspects of Organic Chemistry, 16 November 2006, Kyoto, Japan.

Grants

Murata Y, PRESTO, Japan Science and Technology Agency, October 2005–March 2009.

Murata Y, Grant-in-Aid for Young Scientists (A), April 2004–March 2007.

Murata Y, Academic-Industrial Cooperative Research Fund, April 2006–March 2007.

Awards

Murata Y, Osawa Award, The Fullerenes and Nanotubes Research Society, 8 January 2006.

Murata Y, Young Scientists' Prize, the Commendation for Science and Technology by the MEXT, 18 April 2006.

Murata M, President Prize of Kyoto University, Kyoto University, 20 March 2006.

Synthesis of Selenium-containing Open-cage Fullerene C₆₀

Open-cage fullerene is one of the current synthetic targets of fullerene chemistry besides its well developed exohedral functionalization topic. The ultimate objective for creation of an orifice on the fullerene cage lies in the replacement of conventional methods for the preparation of endohedral compounds and elucidation of their physical and chemical properties. In order to tune the size of the orifice of open-cage fullerenes, we synthesized the selenium-containing open-cage C₆₀ by three-step organic synthesis from fullerene C₆₀. The insertion of molecular hydrogen into the open-cage C₆₀ was achieved in 100% yield under milder conditions compared with those for a sulfur analogue. The kinetic measurements for release of the hydrogen molecule and the X-ray structure analysis revealed that the size of the orifice is larger than that of the sulfur analogue.

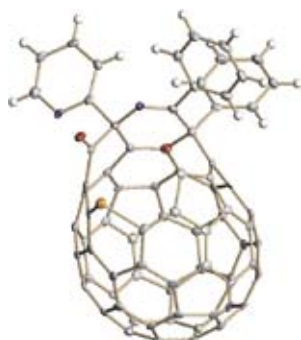


Figure 1. X-ray structure of the selenium-containing open-cage C₆₀.

Encapsulated Hydrogen Molecule as a Sensitive NMR Probe

To examine the effect of encapsulated hydrogen inside C₆₀ upon the reactivity of the outer fullerene cage, the solid-state mechanochemical dimerization of H₂@C₆₀ was conducted. It was found that the dumbbell-shaped dimer, (H₂@C₆₀)₂, was obtained similarly to the reaction of empty C₆₀. Apparently, the inside hydrogen does not affect the reactivity of the outer C₆₀ cage. The ¹H NMR signal for the inside hydrogen was observed as a singlet at δ – 4.04 ppm, which is 8.58 ppm upfield shifted from free hydrogen. Three fullerene derivatives were also synthesized by Bingel reaction, benzyne addition, and Prato reaction in order to further investigate this issue. The NMR signal for encapsulated hydrogen was observed at δ – 3.27 ppm for the Bingel adduct, – 4.30 ppm for the benzyne adduct, and – 4.64 ppm for the Prato adduct. These upfield shifts are quite similar to those reported for the NMR signal of ³He encapsulated in the corresponding derivatives. Thus, the

inside molecular hydrogen of C₆₀ can also be used as a good probe to investigate the chemical reactions at the exterior of the fullerene cage.

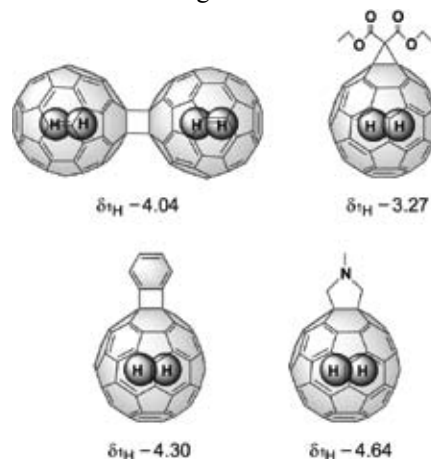


Figure 2. Derivatives of H₂@C₆₀ with the chemical shift of encapsulated hydrogen molecule.

Synthesis of Endohedral Fullerene C₇₀ Encapsulating Hydrogen Molecule(s)

Since the inner space of C₇₀ is larger than that of C₆₀, it might be possible that more than one small molecules be encapsulated. Recently open-cage C₇₀ derivative **1** was synthesized by applying the procedure similar to that used for the synthesis of open-cage C₆₀. Molecular hydrogen was successfully inserted into **1** by treatment with high-pressure hydrogen gas (890 atm) at 200°C. Not only H₂@**1** (97%) but also (H₂)₂@**1** (3%) were found to be formed under these conditions. The complete closure of orifice of H₂@**1** and (H₂)₂@**1** has been achieved via four-step organic reactions without loss of encapsulated hydrogen molecule(s), thus having led to the formation of H₂@C₇₀ and (H₂)₂@C₇₀ for the first time.

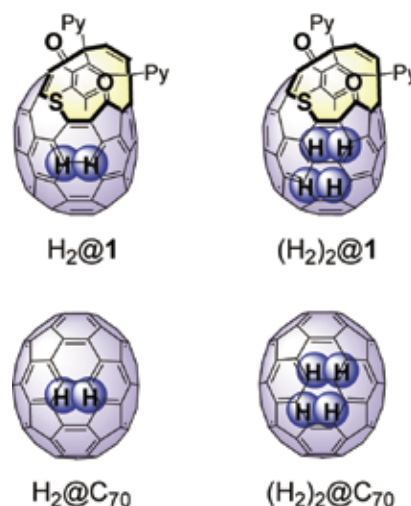


Figure 3. Structures of H₂@**1**, (H₂)₂@**1**, H₂@C₇₀, and (H₂)₂@C₇₀.